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BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 51

USE OF SODIUM SALTS IN THE PURIFICATION OF CLAYS AND IN THE CASTING PROCESS

BY

A. V. BLEININGER, Ceramic Chemist
Bureau of Standards

[ISSUED SEPTEMBER 25, 1915]

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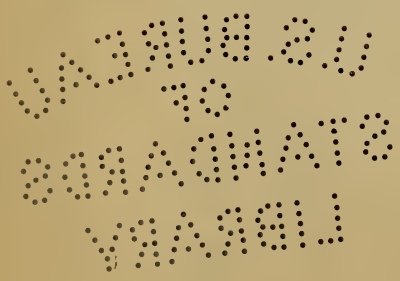

USE OF SODIUM SALTS IN THE PURIFICATION OF CLAYS AND IN THE CASTING PROCESS

By A. V. Bleininger

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I. INTRODUCTION

Clays suspended in water are affected by the presence of small amounts of electrolytes to a remarkable extent. Alkalies tend to hold the clay in suspension in a fine-grained and jellylike mass

(state of deflocculation); acids and salts operate to coagulate and precipitate the material, leaving a clear supernatant solution (state of flocculation). The viscosity of the clay-water system may also be caused to change so that a constant degree of fluidity can be maintained with a low water content by the use of alkaline substances and with a high water content by the addition of acids and salts. The changes in the viscosity of the system make possible the employment of such a process for accomplishing definite industrial objects.

Clays consist of a more or less heterogeneous collection of coarser and finer mineral particles, varying in specific gravity, size, and shape.

The particles of the clay substance proper may be estimated to have a mean diameter of about 0.005 mm with grains possibly as large as 0.01 mm and some so small as to become submicroscopic. Zsigmondy [1] estimates the mean length of kaolin particles to be 0.003 mm. Using the elutriating apparatus, a velocity of the water current of 0.18 mm per second is supposed to remove all of the clay substance. The nonplastic portion of the clay is, as a rule, considerably coarser, though not always, as it is quite possible to have present quartz, ferric oxide, and other minerals in an extremely fine state. The action of the electrolytes concerns chiefly the very finest material and decreases in effectiveness with the size of the particles.

It may be possible, by lowering the viscosity of the clay-water suspension, to bring about a more or less complete separation of the slightly coarser and heavier grains from the more finely dispersed matter, a differentiation which would not be possible without the use of the alkaline reagent. Again, since the principal impurities, the iron-carrying minerals, and the quartz are essentially coarser grained than the clay substance proper, such a procedure would render the elimination of these substances feasible, and hence points out a way toward purifying the kaolins, which constitute the basis of all white ware and porcelain. The principal objection to the use of American kaolins has been the claim that they are not as pure as the corresponding European materials.

[1] Zur Erkenntniss der Kolloide.

It would seem, therefore, a matter of sufficient economic importance to study the effects brought about by the use of alkaline salts in the washing process.

The casting process consists in shaping clay articles of all shapes and sizes by pouring a thick water suspension of the body ingredients (slip) into plaster of Paris molds. The porous plaster at once begins to absorb water from the slip and a coating of the clay body forms on the surface of the mold. After a sufficient length of time has elapsed, depending upon the thickness of wall desired, the remaining slip is poured off, leaving the required shape of the article within the mold. Upon partial drying, the clay body stiffens and shrinks away from the mold so that the piece can be removed and drying completed. By making up a body mixture into a slip with pure water, the resulting shrinkage of the cast piece would be very high, and in the case of heavy articles considerable loss due to checking and cracking would be caused. By the addition of alkaline compounds, usually a mixture of sodium carbonate and sodium silicate, the amount of water required is decreased very greatly and with it the drying shrinkage. The sodium salts, therefore, are necessary for successful casting.

The effect of the alkaline reagents is complex in character and varies with the nature of the clay and the amount of salts added. Increasing proportions of the alkali usually bring about increasing suspension of the fine particles, a condition which reaches a well-defined maximum—complete deflocculation. Further additions tend to reverse the equilibrium and the material is precipitated or coagulated. This may again be followed by another deflocculation phase. Clays carrying soluble salts, like calcium or magnesium sulphate, do not respond readily to the alkaline reagents, because of reaction between the sulphate and the sodium salt.

The present work was undertaken for the purpose of studying the effect of the alkalies upon the behavior of clay suspensions, embracing the materials commonly used in the manufacture of the finer clay products, with special reference to the purification of clays and the casting process.

II. EFFECT OF ALKALIES UPON THE SEDIMENTATION OF CLAYS

1. GENERAL PRINCIPLES

The deflocculating effect of alkali additions to clays may be observed visually by the change in the appearance of the suspension, the holding up of cloudy masses of the material and also by the determination of the viscosity of the clay-water system. Deflocculation corresponds to decreasing viscosity and the maximum stage coincides with minimum viscosity.

The differences obtaining between the conditions of the settling of clay in water and in such an alkaline solution may be readily illustrated by placing equal amounts of the same kaolin in two glass tubes and adding to one ordinary water and to the other the same volume of a solution carrying the proper amount of alkali required to bring about complete deflocculation. In the tube containing the water, sedimentation of the coarser particles will be observed, but the amount of coarser material thrown down will be less than in the case of the alkaline solution. Likewise, the precipitated granular matter, in the case of the water, will be found to contain more or less fine clay matter carried down mechanically, while the alkaline solution brings about a clean, sharp separation between the two kinds of material.

Again, while the clay-water suspension may still carry particles of iron-carrying minerals, like larger flakes of biotite mica, these have been settled in the deflocculating solution.

By comparing a drop of the alkaline suspension under the microscope with a drop of the ordinary water slip the former will be found to contain a far greater number of particles showing Brownian movement. Evidently the alkali has been active in increasing the dispersion of the clay substance. Upon adding to the alkaline suspension an amount of acid greater than that required for neutralization coagulation will take place. The cloudy mass will be precipitated to the bottom of the tube and the supernatant solution will appear clear. The Brownian movement of the particles will have diminished greatly because of their larger size.

The prompt settling of the granular particles brought about by the decreased viscosity of the system is explained by the fundamental relation expressed by Stoke's law

$$v = \frac{2\ r^2\ g}{9\ k}(d - d_1)$$

where v = velocity of settling, r = radius of particles, k = viscosity, d_1 = density of fluid, d = density of particles, and g = gravity constant, in which the viscosity factor is evidently of prime importance.

The physical changes of the suspension are quite complex, however, for if dispersion is the principal function involved, it must be assumed that the fine grains of clay already present should be still further subdivided into submicroscopic particles, resulting in a certain amount of lyophile, emulsoidlike substance. Indeed, by filtering an alkaline clay suspension through paper such a material may be separated. This pseudoemulsoid may play an important part in such a suspension, tending to prevent further decrease in viscosity and to hold up fine particles which otherwise might tend to settle.

It is quite well understood by this time that the "liquefying" action of the alkaline salts, sodium carbonate, and sodium silicate upon clay is due to the action of the OH' ions present in the solution. Both sodium carbonate and sodium silicate are strongly hydrolyzed, containing an excess of hydroxyl ions, according to the state of the equilibrium, the temperature, and the extent to which the Na ions are absorbed. Sodium carbonate in solution is completely ionized into 2 $Na^{\cdot}$ and CO_3'' ions, and these react with the OH' and the $H^{\cdot}$ of water to form sodium hydroxide and carbonic acid, respectively. Similar hydrolysis occurs with the sodium silicate. The negatively charged OH' ions repel the similarly charged clay particles electrostatically. Repulsion may take place only when the electrical charges of the particles are approximately equal. This increases the state of dispersion of the system, breaking up the larger particles into smaller ones. Hence the water penetrates more deeply into the clay structure and causes the clay to "liquefy." The maximum amount of deflocculation is brought about by a definite concentration of OH' ions, and if

exceeded, "stiffening" will again take place, during which period the alkalinity decreases. This stage may again be followed by a second liquefaction, due to absorption of the salts. Organic colloids appear to act somewhat similarly to the sodium salts in bringing about increased dispersion; but at the same time the latter seem to protect the particles against flocculating cations, so that the suspension is less sensitive to the action of coagulating salts. The alkaline, fluid, casting slip without the presence of sufficient amounts of organic colloids is at once changed to the stiffened condition by the introduction of salts like the sulphates or chlorides of calcium, magnesium, or aluminum. The presence of such salts in the clays, therefore, requires not only an increased amount of alkali to bring about deflocculation, but may even render the maximum liquefaction impossible.

2. USE OF ALKALINE COMPOUNDS IN THE WASHING OF CLAY

The principal impurities in clay are the minerals, quartz, feldspar, siderite, pyrite, ilmenite, biotite mica, and ferric oxide. The first five usually occur in granular form, while the biotite mica is found in flakes more difficult to separate; the ferric oxide, usually hydrated, may be present entirely as a colloid. The last impurity, especially in the case of very fine-grained clays, offers the greatest difficulty in separation, and the task quite often is hopeless, owing to the fact that this material becomes part of the colloidal structure of the clay itself.

In employing alkaline reagents in the washing of clay the process employed need not conflict with the ordinary washing process as now practiced.

The clay material would be blunged up as is now being done, but in place of the water there would be used a very dilute solution of caustic soda or of sodium carbonate and sodium silicate (water glass), in equal parts. The amount of soda in this solution should correspond to the amount required to bring about complete deflocculation. The amount of reagents to be added depends upon the percentage of yield and the character of the clay. The quantity necessary can be determined, however, with sufficient accuracy, so that for each ton of crude clay a definite amount of the alkali compound can be added. After the slip has

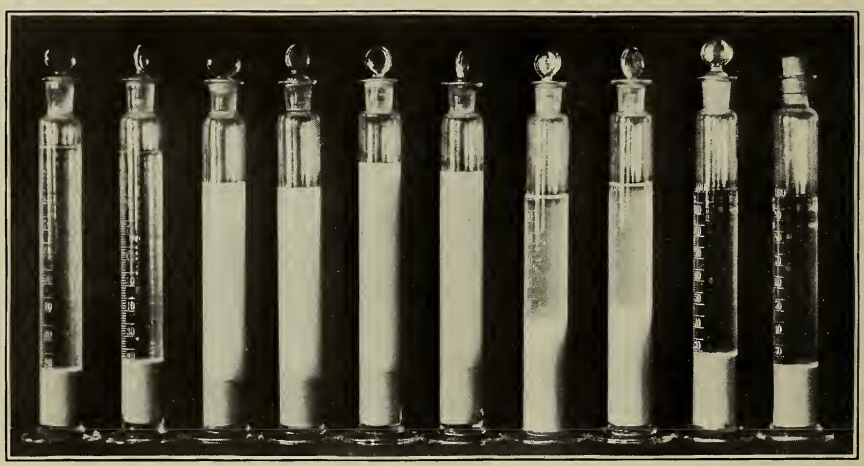

FIG. 1.—*Effect of increasing amounts of NaOH in bringing about deflocculation and reflocculation*

passed through the settling troughs and has been screened and collected in the settling tank it is allowed to stand.

The finer impurities—fine grains of silica, biotite mica, etc.—will now settle. The time of settling governs the degree of purification attained. Longer standing naturally precipitates more of this material than short standing. After a sufficient period the slip is now run into another tank where it is coagulated for the purpose of filter pressing, because the alkaline condition, with the accompanying degree of dispersion into exceedingly fine particles, would tend to clog the filter cloth, and also would cause the press water to run off turbid. At the same time the efficiency of the process would be greatly decreased on account of the slowness of filtration. In the second tank the coagulating reagent, usually aluminum sulphate, is introduced, whereupon the clay will settle out in a curdled mass, which is pumped to the filter press. This precipitation can not be carried on in the first settling tank for the obvious reason that the coagulated clay would mix with the imputities which have been settled out.

The amount of alkaline reagent to be used depends upon the character of the clay. In the materials investigated so far in this laboratory the amounts varied from about 0.05 to 0.2 per cent, or from 1 to 4 pounds per ton of dried clay. The actual cost of the reagent, therefore, should be trifling and should not exceed 7 to 8 cents per ton, including the cost of the aluminum sulphate used for coagulation. Too great an addition might entirely nullify the action. It is important, therefore, that in each case the proper amount of alkali be determined by the use of the viscosimeter, or by means of a series of glass settling tubes in which the degree of deflocculation is readily observed. In Fig. 1 the effect of increasing amounts of caustic soda upon fuller's earth is shown, representing the phases of coagulation, deflocculation, and again of coagulation after standing for 12 hours.

In rare cases, as with certain Missouri fire clays, sodium oxalate has been found to be more effective than the alkaline compounds mentioned above, but the method of procedure is the same.

It is evident from the nature of the process that the greater purity of the clay is obtained at the expense of an increased amount of residue or waste, a fact which must be taken into con-

sideration in the commercial application of such a process. So far the writer knows of only one American washing plant making successful use of the principles involved here, and our own work is based on experiments carried on in the laboratory and with comparatively small amounts of material. It would seem, therefore, that experiments should be conducted on a larger scale. This laboratory would be pleased to be of assistance in helping to carry out such work on a commercial scale.

III. RESULTS OBTAINED IN TREATING SEVERAL CLAYS

1. GEORGIA KAOLIN

It was thought desirable to subject some commercial clays used in the pottery industry to the process here described in order to determine the difference between the treated and the untreated materials. These clays, with the exception of the ball clay, had been previously washed by the customary process and represented commercial shipments.

Porcelain bodies in which the clay substance was partly introduced, as a certain brand of Georgia kaolin, were found to contain particles of impurities which were very objectionable. It was also known that the same clay had been giving trouble in one pottery because of the introduction of black specks. Some shipments of the kaolin were more objectionable for this reason than others, the washing process employed at the mine in question being somewhat erratic.

A 25-pound sample of the Georgia kaolin was taken from stock and blunged in a large ball mill for several hours. Portions of the slip were placed in 500-cc bottles and caustic soda in amounts varying from 0.05 per cent to 0.25 per cent was added to the respective bottles. The bottles were thoroughly shaken and allowed to stand for one-half hour. In this way it was determined that an addition of 0.17 per cent of caustic soda produced dispersion such that the clay slip attained maximum fluidity and an accompanying rapid settling out of the coarser particles.

The slip was placed in a large stoneware jar, 0.17 per cent of caustic soda by weight added, and the slip thoroughly stirred. After allowing to settle for one-half hour the material in suspension was siphoned off, passed through a 150-mesh sieve, aluminum

chloride added, and the flocculated material filter-pressed. Disks 10 cm in diameter were made by pressing the rewashed kaolin in plaster molds. For purposes of comparison disks were also prepared from the kaolin as received from the clay dealers. Bodies having a composition of 50 per cent clay, 30 per cent flint, and 20 per cent spar were made up from the kaolin and the unwashed material and molded into 10-cm disks.

The test pieces molded from the kaolin and from the bodies were fired, unglazed, to cone 10 in closed saggers. The test pieces molded from the rewashed kaolin and the body containing the rewashed kaolin were markedly superior in color and freedom from specks to those molded from the kaolin taken from stock and not rewashed.

2. NORTH CAROLINA KAOLIN

The deflocculation tests on Georgia kaolin were duplicated on a sample of North Carolina kaolin taken from stock in the same manner, the quantity of caustic soda necessary to produce the desired dispersion being about 0.19 per cent. Test pieces were molded as before and fired to cone 10. The North Carolina kaolins appear to respond more quickly to the action of the alkali, the coarser material settling out rapidly.

Although the North Carolina kaolin produced a whiter color than the Georgia and contained fewer particles of dark-burning impurities, a noticeable improvement in color and cleanness was evident in the test pieces molded from the rewashed material.

3. FLORIDA KAOLIN

Florida kaolin appears to respond less readily to the action of the alkali than either the Georgia or North Carolina kaolins. The deflocculation tests were conducted as before on a sample purchased on the market. The amount of alkali added was 0.14 per cent, but some difficulty was experienced in determining just what quantity to use. The Florida kaolin usually produces a very good white color, although sometimes it may contain dark-colored impurities which produce objectionable specks in the finished piece.

The test pieces produced from the rewashed kaolin and fired to cone 10 were slightly improved in color and were markedly free from the black specks brought out in the test pieces molded from the clay as received from the dealer and without rewashing.

4. TENNESSEE BALL CLAY NO. 3

In addition to the characteristic cream or buff color produced in the burning of ball clays, dark-colored specks, due to the presence of particles of impurities, are in evidence. On account of the great plasticity and the consequent difficulty of washing, ball clays are placed on the market in the crude state. In addition the washing of ball clays is discouraged, owing to the supposed decrease in plasticity accompanying the washing process.

The washing tests on the Tennessee No. 3 ball clay were conducted in a manner somewhat different from that for the kaolins. The ball clay was ground, screened, and blunged in a ball mill for a short time. To the mill charge 0.4 per cent by weight of hydrochloric acid was added and the blunging continued for several hours. The slip was placed in a stoneware jar and allowed to settle. The supernatant liquid was then siphoned off and discarded and the clay again blunged with a supply of fresh water, to which was added 0.15 per cent by weight of caustic soda. After standing for one hour the suspended matter was siphoned off, flocculated by an addition of aluminum chloride, and filter-pressed.

A number of 10-cm disks were molded from bodies composed of 50 per cent ball clay, 30 per cent flint, and 20 per cent feldspar, the washed ball clay being used for one body and the crude ball clay for another. The disks were fired to cone 9 in closed saggers.

The body prepared from the washed ball clay, although showing the characteristic buff color of this type of clay, was much improved as regards cleanness of color and freedom from specks of iron-bearing minerals. The buff color was also slightly lightened in the bodies prepared from the rewashed clay.

Means of measuring the increase or decrease in plasticity of the washed ball clay were not at hand, although so far as could be observed from the working qualities of the two materials there was but small difference in plasticity.

5. GENERAL EFFECT OF DEFLOCCULATION UPON COLOR

Obviously in most cases the degree to which the color and general appearance of a clay is improved by the employment of deflocculating agents is a factor of the original purity of the clay and the excellence of the washing treatment to which it is submitted at the washing plant. Clays occur, however, which, although of poor color, can not be improved by the employment of deflocculating agents on account of their physical constitution.

Washing tests on samples of English kaolins to which deflocculants were added did not produce noticeable improvement in color, owing to the original purity of the materials or the excellence of the washing treatment. Of the three varieties of American kaolins subjected to the deflocculating treatment, as stated before, the Georgia kaolin showed the greatest improvement as regards color. The improvement in the North Carolina and Florida kaolins was not so noticeable, although the gain was well worth the expense of the treatment.

6. EFFECT UPON DRYING AND BURNING SHRINKAGES

The drying and burning shrinkages of the kaolins and bodies are affected somewhat by the use of deflocculating agents. The average shrinkage measurements in the following table were made upon 10-cm disks, which were prepared from the kaolins and bodies by pressing in plaster molds. The disks were dried at 110° C and fired in saggers to cone 10.

TABLE 1

Shrinkages (in percentages of dry length) Cone 10

Kaolins	100 per cent clay		50 per cent clay, 30 per cent flint, and 20 per cent feldspar	
	Drying shrinkage	Burning shrinkage	Drying shrinkage	Burning shrinkage
Florida kaolin, as received	7.55	12.45	5.45	7.90
Florida kaolin, washed	7.30	12.70	4.75	9.15
North Carolina kaolin, as received	4.75	5.40	3.05	7.40
North Carolina kaolin, washed	3.70	6.92	2.20	8.75
Georgia kaolin, as received	4.60	12.75	4.05	9.45
Georgia kaolin, washed	3.90	15.20	2.60	9.10

It will be noted that the addition of the alkali caused a decrease in the drying shrinkages of the test pieces containing the kaolins which were subjected to the washing treatment. This decrease is most noticeable in the body containing the washed Georgia kaolin.

Treating the kaolins with the electrolyte, however, increases the burning shrinkage of the test pieces, with the exception of the body containing the Georgia kaolin. This increase in burning shrinkage is due to the removal of the fine-grained, nonplastic materials from the kaolins and the presence of a proportionately greater amount of clay substance.

IV. ELECTRICAL SEPARATION OF CLAY

1. GENERAL DESCRIPTION

A new electrical process for the purification of clay, invented by Count Schwerin,[2] in Germany, is causing widespread interest. The treatment consists in stirring up the clay with water and removing the coarse material by means of screens and settling. A previously determined amount of electrolyte is added and the suspension conveyed to the osmosis apparatus, which is in the form of an endless metallic belt upon which the purified clay is deposited. The clay is scraped off and conveyed to the dryers. It is claimed that the product contains only 25 per cent of water and is free from pyrites, sand, or other impurities, has a lower alkali and higher alumina content, and is greatly improved in color, plasticity, bonding power, refractoriness, and uniformity.

It was thought desirable to examine the principle under which this process operates, and to carry on a few experiments intended to bring out more clearly some of the factors involved.

2. THEORY OF PROCESS

Small particles in suspension between two electrodes will move under the influence of a direct current either to the cathode or the anode. This phenomenon is called kataphoresis. Suspended particles of shellac, clay, quartz, cotton, silk, starch, graphite, sulphur, etc., travel to the positive electrode. The suspended

[2] Tonindustrie Zeitung, 36, pp. 1283–1285; Trans. English Cer. Soc., 12, Part I, pp. 36–65.

particles are always electrically charged and, according to the + or − character and the magnitude of the charge, they migrate to the negative or the positive pole. In pure water most substances are charged negatively. Water itself is positive in electroendosmosis and moves toward the negative pole. No electro-osmotic effects are noted in liquids like chloroform, ether, petroleum, oil of turpentine, etc. The addition of very small quantities of electrolytes to solutions used in kataphoresis may promote endosmosis or oppose it. Larger additions of any electrolyte cause the action to cease entirely. According to Freundlich [3] "it is to be expected that the addition of OH′ ions to a negatively charged particle would raise the kataphoretic migration velocity to the positive pole, while acids and cations of higher valency would decrease it with increasing concentration, reduce its value to zero, and finally change its sign With small particles, positively charged, the OH′ ion and the anions of higher valency are active in the same direction." Clay containing a considerable content of soluble salts should therefore be expected to respond poorly. Whitney and Blake [4] found that upon adding 0.004 normal nitric acid solution to colloidal silver the particles originally migrating to the positive pole reversed their direction. A similar reversion was shown upon the addition of aluminum sulphate.

It is evident that the effect of the additions of electrolytes is intimately connected with the flocculating action of the salts.

The velocity of migration of fine particles seems to be independent of their size and shape within certain limits. It is interesting to note that this velocity does not differ considerably from the value given for the more inert ions like sodium. While for the latter the velocity constant is 43×10^{-5} cm per second, for a drop in potential of 1 volt per centimeter, the velocity of quartz particles, averaging 0.001 mm in diameter, is 30×10^{-5} cm under the same conditions. There appears to be no direct relation between the amount of clay separated and the current used, and the separation is hence not governed by Faraday's law.

[3] Kapillarchemie, p. 239.

[4] Jour. Am. Chem. Soc., 26, p. 1339.

3. STAGES OF ELECTRICAL SEPARATION

The process of electrical purification may be said to consist of three operations—the blunging and screening of the clay, the treatment with electrolyte, and the separation upon the positive electrode. It is evident that the washing process in itself accomplishes a great deal in removing impurities such as sand, feldspar, pyrites, etc. To afford strict comparison between the washing process and electrical purification it is not fair to compare the crude with the electrically treated material. The difference between the washed clay and that treated by the new process must be used to establish the merits of the case.

The additional separation brought about by the use of an electrolyte is really the most important factor in the scheme. By the proper treatment with small amounts of chemicals the viscosity of the slip may be decreased so that considerable quartz and feldspar, ordinarily held in suspension, may be thrown down. The suspended material thus remaining is of course of greater purity, and the deposit attached to the electrode should therefore be clay of better grade than that which is obtained by the ordinary washing, as has been shown in previous paragraphs.

It is obvious that the same treatment can be applied where the slip is to go through a filter press, there being needed only adequate tank facilities for the separation of the suspended matter. The electrical treatment itself has very little to do with the purification, since the coarser impurities have already been removed by the previous precipitation treatment. The manner of deposition upon the electrode is of a mechanical character and takes the place of filter-pressing, having of course the advantage of being continuous and automatic. Other methods of separating the clay from the water might be employed, such as the Sweetland system of filter-pressing, the economy of which should approach ideal conditions.

4. RESULTS OF ELECTRICAL SEPARATION EXPERIMENTS

In the present work it was thought advisable to collect further information (1) in regard to the reagents most suitable for the treatment preliminary to the actual separation and the determi-

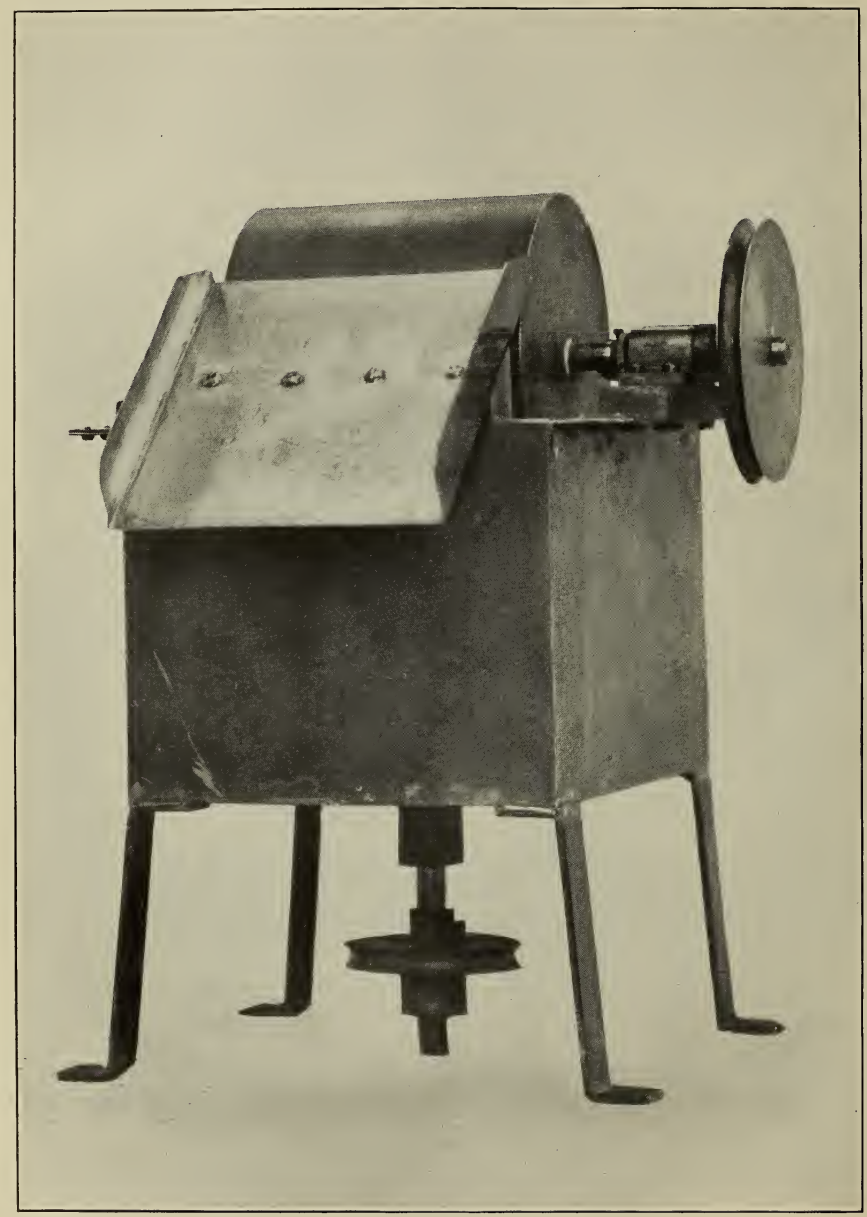

FIG. 2.—*View of electrical separating apparatus*

nation of the proper amount to be used; (2) in regard to the behavior of different materials such as quartz, feldspar, ferric oxide, and several types of clay when subjected to the electrical treatment.

It was found, in agreement with Ashley's work,[5] that sodium hydroxide and sodium oxalate are the most effective reagents, the former to be used in the majority of cases, while the second substance is particularly suitable in the case of certain fire clays. For the purpose of determining the proper amount of the reagent, viscosity determinations by means of the efflux tube were found most convenient. The method of procedure was to add small quantities of NaOH to the slip, making viscosity readings until the minimum point of the curve was reached. This consistency proved to be the most suitable for the electrical separation. In cases where the sodium hydroxide was found to be less effective resort was had to the use of sodium oxalate, $Na_2C_2O_4$. In this simple manner the proper conditions are readily obtained. Indiscriminate additions of chemicals will lead to misleading results and unsatisfactory separation. The amount of the reagent necessary is small and never exceeds 0.2 per cent in terms of the dry weight of the clay. An excess of the reagent must be avoided in all cases.

The work dealing with the electrical separation of suspended materials was mostly done by means of a very simple apparatus. A 220-volt direct current was available, controlled by two water rheostats. The separating receptacle was a copper can 6 inches in diameter and 5 inches high. This was filled with the slip, and a flat carbon electrode was just immersed. Electrical connections were made with the can and electrode. The latter was a carbon plate of which there was a stock on hand. In the commercial apparatus it is said that the positive electrode consists of type metal, though aluminum or other metals may be used. By means of a volt and ammeter the current was under observation.

For handling larger quantities of material an automatic apparatus was built (Fig. 2) consisting of a copper tank 5¾ by 6½ by 7¼ inches, in which a revolving drum 5 inches in diameter and 4¾ inches wide, insulated from the tank, was used as the positive

[5] Bureau of Standards, Technologic Paper No. 23.

electrode. The negative electrode consisted of two insulated metallic strips beneath the roll. The clay adhering to the surface of the drum was scraped off at the opposite side. A slow-moving stirrer was also provided at the bottom of the tank to prevent undue separation. A flush hole was arranged for washing out the residue after each run.

In the following paragraphs the results obtained in the electrical separation of several materials are described.

Flint.—Finely ground flint was found to separate well, forming a dense layer at the positive electrode with voltages varying between 125 to 180 and a current strength of 0.75 ampere. With this material the deposition upon the electrode was most satisfactory without the addition of any electrolyte.

Feldspar.—With a sample of Brandywine feldspar, which was rather coarsely ground, practically no separation took place with or without electrolyte. Using Maine feldspar deposition occurred, but not as marked as with the flint. The voltage used was 160, with 0.75 ampere. The addition of electrolytes produced no increase in yield.

Ferric Oxide.—Finely divided ferric oxide in suspension formed no deposit with or without electrolyte. An addition of 6 per cent of this oxide was then made to North Carolina kaolin, and the treatment carried out upon this mixture. Upon determining the ferric oxide in the original mixture and in the portion separated on the electrode, it was found that no reduction whatever in the iron content was accomplished. All of the ferric oxide admixed with the kaolin was carried along with the clay particles.

Kaolin.—In order to determine whether further purification could be brought about with washed clays, runs were made with the North Carolina and Florida kaolin. In both cases heavy firm deposits were obtained with a content of 0.2 per cent caustic soda with voltages varying from 80 to 160. Practically all matter in suspension was carried to the electrode. The densest layer is obtained with the highest voltage.

Impure Fire Clay.—A fire clay of the No. 3 type, from Aultman, Ohio, was ground to pass the 40-mesh sieve and made into a slip showing minimum viscosity with 0.1 per cent caustic soda. The separation took place very satisfactorily. Upon making briquettes

from the original clay, the separated portion, and the residue, the linear drying shrinkages were found to be 8.4, 7.5, and 6.25 per cent, respectively. Upon burning the specimens to cone 9 in a sagger the separated portion was decidedly superior in appearance, showing a uniform light-gray color, while both the original clay and the residual part were darker and showed numerous black spots.

In connection with these experiments the reverse effect, that of the negative electrode upon plastic clay, was briefly verified. Upon making a steel trowel the negative pole, it was found that water was drawn from a mass of plastic clay into which the tool was inserted and thus caused the latter to penetrate very readily. This confirms the results reported in a paper before the National Brick Manufacturers' convention of 1912 at Chicago.

5. GENERALIZATION, BASED ON RESULTS OBTAINED

With the general run of clays the suspended clay will be deposited by the electrical current just as it is, and if it has not been subjected to the sedimentation process mentioned the quality of the product will not be superior to that of ordinary washed clay. The desired results can be obtained by the chemical washing process first described with the use of the filter press without resorting to the use of electricity. However, if the electrical continuous separation can replace the filter press economically its use would be justified. At the present time no exact figures are available for purposes of comparison. To a large extent it would be a matter of the comparative economy of the electrical endosmose apparatus and the filter press. If the latter should be improved, as has been done in the so-called clamshell press, it is quite possible that the economic advantage might remain with the filter press.

V. FUNCTION OF THE ALKALIES IN THE CASTING PROCESS

1. VISCOSITY OF SLIPS

The principal effect of the alkaline additions to a casting slip is to decrease the amount of water required to hold unit weight of clay in the suspended state with sufficient fluidity to permit of pouring.

The practical aim in casting evidently must be to increase the weight of clay body carried by unit volume of the water to the maximum. From 29.5 to 30.5 ounces per pint is the usual weight to which casting slips are carried in the case of white vitreous bodies. It is evident that the content of clay and nonplastic additions bring about variations in this respect. At the same time the composition of the body should be of such a nature that proper drainage of the water from the stiffening mass to the mold may occur. The effect of the alkaline reagents added to a slip is followed most readily and quantitatively by the determination of the viscosity. For this purpose various types of flow or torsion viscosimeters may be employed. Owing to the coarse nature of the suspensions the accurate flowtubes of Ostwald are out of the question, and exceedingly simple devices like the brass efflux tubes illustrated in Fig. 3 may be used. Here the time required for a given volume of slip, say 200 cc, to flow through an orifice 5/32 inch in diameter is determined. The effect of the varying head due to the lowering of the level of the liquid is largely overcome by the employment of Mariotte's principle of the immersed tube. It is necessary for the proper working of the device that all joints be made air-tight. By determining the time required for the flow of water at 18° C, and dividing the observed time for the same volume of slip by this constant quantity, the viscosity of the suspension in terms of water is readily computed. For the technical determinations in question, corrections such as are necessary in the use of the Ostwald viscosimeter are not required. It was likewise found that corrections for temperature are negligible.

Of the torsion viscosimeters the Coulomb and Couette instruments are available, while for accurate results expressed in absolute units the Clark viscosimeter renders good service. The Couette apparatus represents probably the most satisfactory one for determining relative viscosity. It consists of a vessel rotating at constant speed, which contains the liquid. A metal cylinder suspended by means of a wire is immersed in the suspension. The torsion exerted upon the wire may be measured by means of a mirror attached to the projection of the cylinder to which the wire

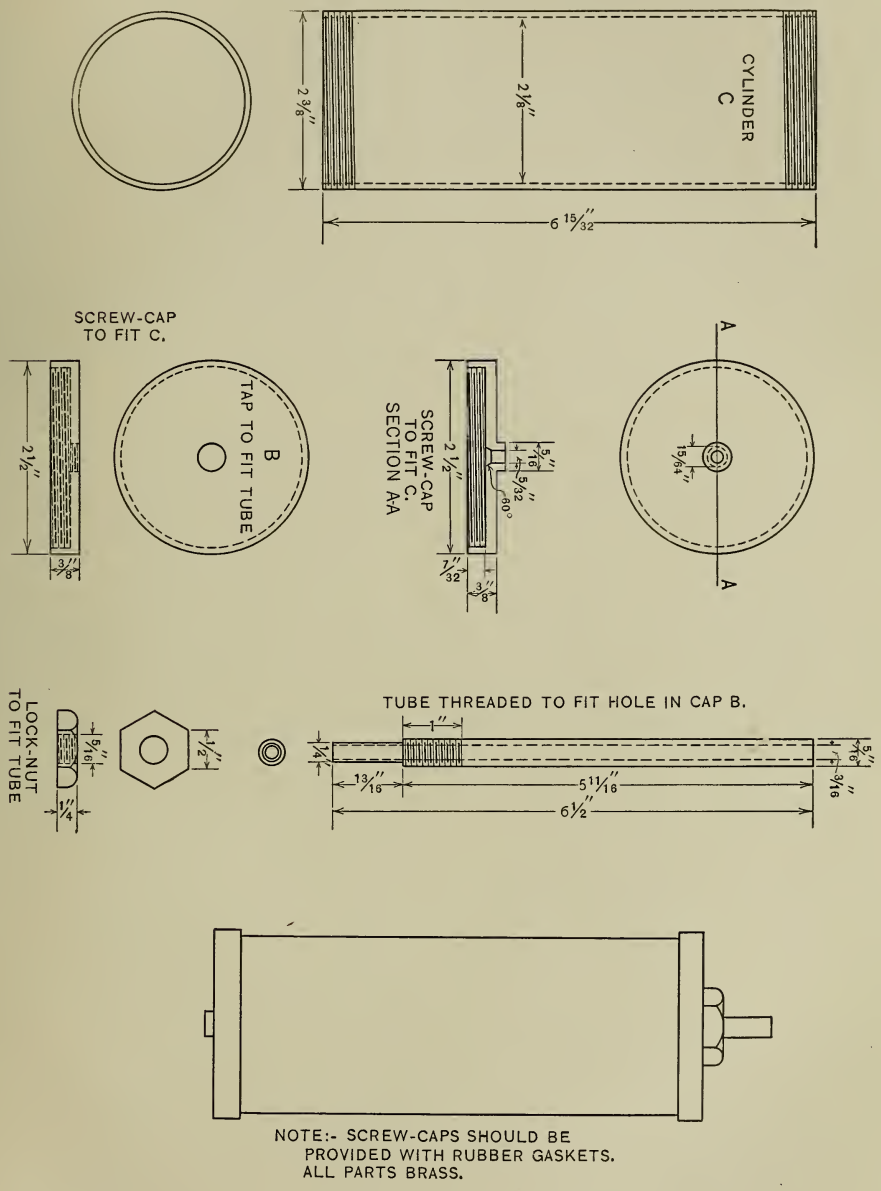

FIG. 3.—*Design of brass viscosimeter*

is attached and the angular deflection noted upon a graduated scale at a suitable distance from the instrument. Various investigators, like Hatschek and others, have found this apparatus very suitable in their investigation of colloids. The flow viscosimeter as used in this work, is sufficiently accurate for purposes of comparison and has the advantage of being simple and cheap.

In the study of dispersed systems of any kind the viscosimeter may be considered as important as the voltmeter and ammeter in the measurement of electrical quantities.

In general, the viscosity of a disperse system may be said to correspond to the relation suggested by Einstein, Hatschek, and others,

$$n_1 = n_2\left(1 + K\frac{v_1}{v}\right)$$

where n_1 = viscosity of the system,
n_2 = viscosity of continuous phase (water in case of clay slip),
v_1 = volume occupied by colloidal particles,
v = total volume,
K = constant.

In many colloidal systems the value of the constant has been found by Hatschek to approximate 4.5 for small concentrations. Owing to the large amount of comparatively coarse material in clay and body suspensions, the Hatschek constant of the above equation can not be expected to hold for systems of this kind, but is certain to vary with the different materials. In the case of Florida kaolin it was found to be 5.05 for small concentrations. Using this relation, it is assumed, of course, that the conditions of the system are practically in equilibrium, as time, temperature, absorption, and other factors are likely to bring about changes in the viscosity without change in the volume relations of dispersing medium and dispersed matter.

The medium which holds up the nonplastic matter in casting slips must be considered to consist of a pseudoemulsion, resulting from the further breaking down of the finer clay particles. It is essential that the viscosity of the slip be maintained sufficiently high by the use of enough clay to prevent separation, which is likely to occur, in agreement with Stoke's law.

It is easy to see that the use of comparatively coarse clays, resulting in an insufficient amount of the emulsoid substance, while draining readily, might give rise to difficulties due to separation. The viscosity of a clay suspension supposedly in equilibrium, and with it all accompanying properties, are not maintained constant. Variations occur with a number of factors, as temperature, time, and change in the concentration of the dissolved salts due to absorption, solution, or reaction. Clays, of course, differ widely also in their response to the action of the alkalies. The physical structure (fineness) of clays and their chemical composition with special reference to the content of soluble salts, cause them to behave differently. The previous mechanical treatment of the clay, as by washing or drying, is also of considerable influence.

2. OUTLINE OF WORK

The present work deals with the following topics:

1. The effect of increasing amounts of Na_2CO_3 and Na_2SiO_3 upon the viscosity of four body slips in which the feldspar and flint are kept constant at 21 and 34 per cent, respectively, and 45 per cent clay is introduced in succession by North Carolina kaolin, Georgia kaolin, Florida kaolin, and Tennessee No. 3 ball clay. The sodium silicate used contained in the dried state 70.3 per cent SiO_2 and 29.7 per cent Na_2O, corresponding to the formula $Na_2O.2.44SiO_2$, which is to be understood when mention is made of sodium silicate throughout this paper.

2. The effect of various proportions of North Carolina kaolin body upon each of the three other bodies, with reference to the viscosity of the resulting mixtures.

3. The absorption of Na_2CO_3 and NaOH by Florida and Georgia kaolins.

4. Tensile strength of bodies cast under different conditions of consistency and viscosity.

5. Calculation of constant in general viscosity formula for different concentrations of Florida clay slips.

6. Effect of time on change of viscosity of casting slips.

VI. EFFECT OF VARIOUS AMOUNTS OF SODIUM CARBONATE AND SODIUM SILICATE

1. NORTH CAROLINA KAOLIN BODY

This mixture was made up to a slip containing 59.73 per cent of solids. The viscosity was determined by means of the efflux tube

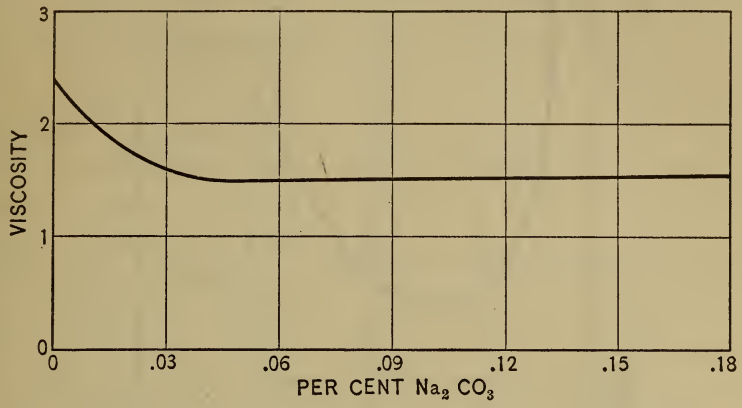

FIG. 4.—*Effect of sodium carbonate on North Carolina kaolin body*

already described. Two series of tests were run, one with increasing amounts of sodium carbonate and one with sodium silicate.

The Na_2CO_3 tests are shown in the diagram of Fig. 4. From

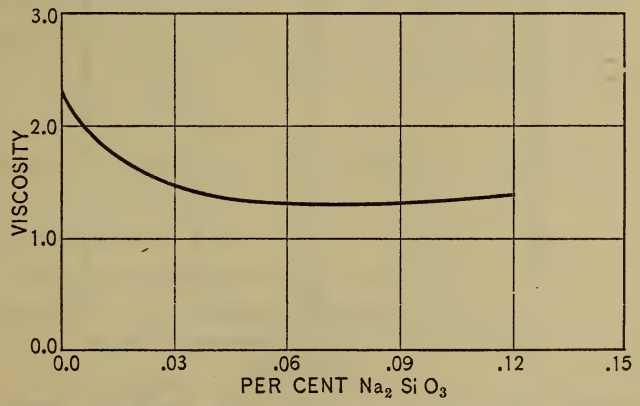

FIG. 5.—*Effect of sodium silicate on North Carolina kaolin body*

this curve it is seen that there is no very large drop in viscosity and that the minimum is reached with 0.045 per cent of the reagent. No tendency toward a maximum point is noted. This illustrates very nicely the deficiency in the amount of pseudo-

emulsoid resulting from the use of this clay, owing to its comparatively coarse nature. Either the amount of highly dispersed material is quite small or all the grains are too coarse to be affected decidedly by the reagent employed.

Sodium Silicate Series.—In this case (Fig. 5) similar conditions

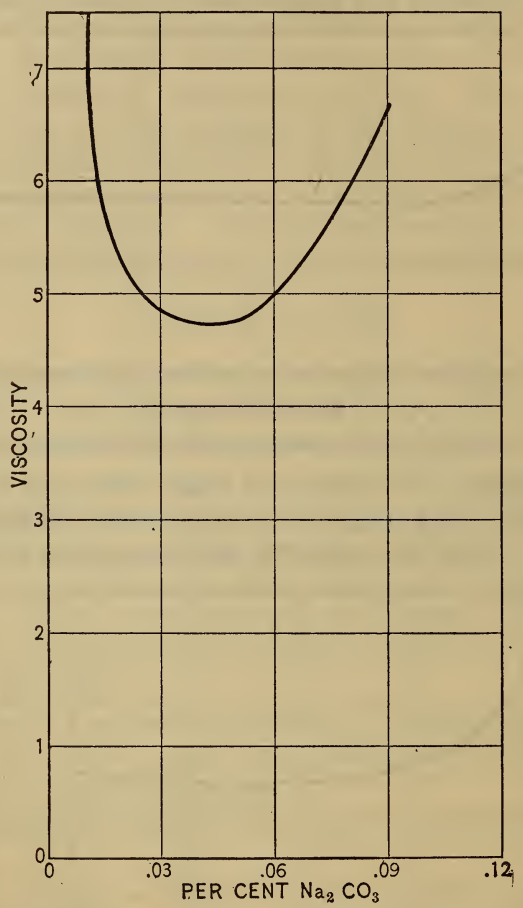

FIG. 6.—*Effect of sodium carbonate on Georgia kaolin body*

prevail and the minimum point is likewise reached with 0.045 per cent. The drop in viscosity is from 2.35 to 1.30. It appears, therefore, that owing to the comparatively coarse dispersion of this kaolin the system is not greatly influenced by the alkali reagents.

2. GEORGIA KAOLIN BODY

Sodium Carbonate Series.—The slip used for both series contained 61.38 per cent solids. From Fig. 6 it appears that the initial viscosity is very much greater than in the case of the North Carolina kaolin body. The value was above 7, but could not be determined accurately owing to the thickness of the slip. A content of 0.03 per cent Na_2CO_3 at once lowered the viscosity to 4.75, reaching a sharply defined minimum. With more than 0.045 per cent of the reagents the viscosity at once increases. This kaolin therefore is very sensitive to changes in the alkali concentration, and hence requires greater care in regard to this point.

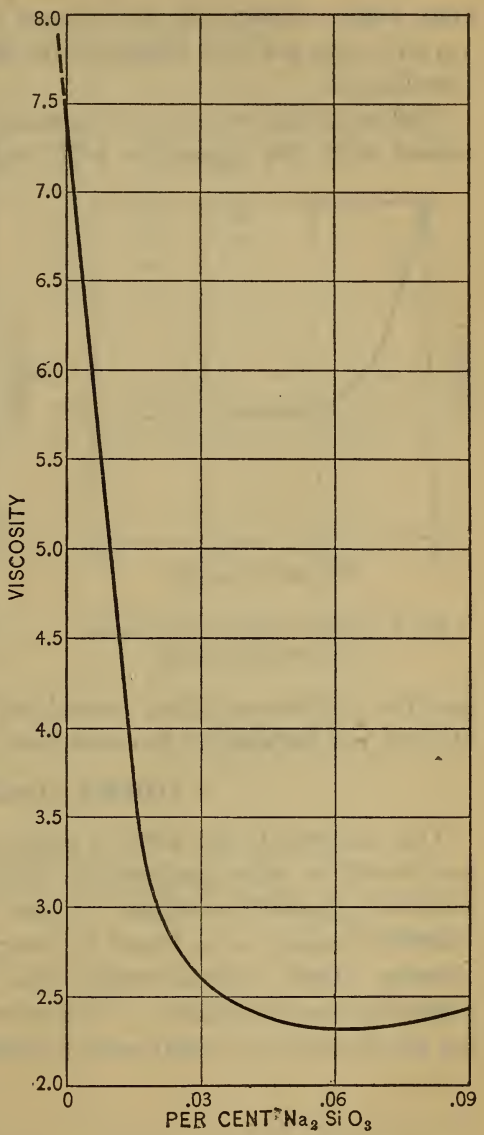

FIG. 7.—*Effect of sodium silicate on Georgia kaolin body*

Sodium Silicate Series.—In this case (Fig. 7) the minimum viscosity, 2.3, represents a considerably greater drop in viscosity than is the case with the carbonate. This reagent is therefore very much more effective. Although the tendency of the curve toward an increase in viscosity is clearly shown, the change is very much less abrupt than in the first case and the range of minimum viscosity considerably wider.

3. TENNESSEE BALL CLAY BODY

Sodium Carbonate Series.—The slip as used contained 47.68 per cent solids. From Fig. 8 it is seen that the drop in viscosity is 1.9 with 0.03 per cent reagent, and that no well-defined minimum is indicated.

Sodium Silicate Series.—Practically the same results are obtained with this reagent as with Na_2CO_3 (Fig. 9). It is evident

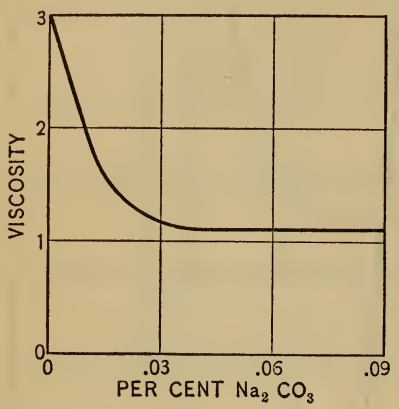

FIG. 8.—*Effect of sodium carbonate on Tennessee ball clay body*

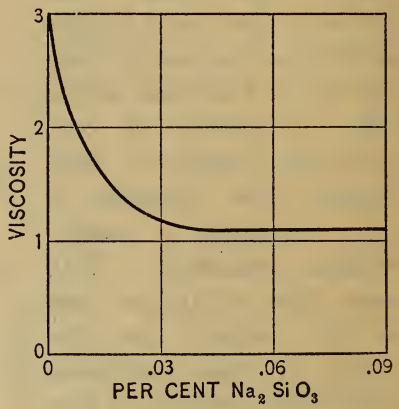

FIG. 9.—*Effect of sodium silicate on Tennessee ball clay body*

that the alkalies are being neutralized by the salts of the ball clay, but not yet sufficiently to cause flocculation.

4. FLORIDA KAOLIN BODY

This material in the form of a slip containing 50 per cent solids was found to offer considerable difficulty in regard to obtaining constant viscosity readings. Upon making check readings the viscosity values were found to drop off continually. With increasing alkali concentrations this change seemed to become somewhat less prominent. This point may be illustrated by giving the figures for several sets of determinations, Table 2.

TABLE 2

Viscosity with Increasing Amounts of Na_2CO_3

0.03 per cent	0.06 per cent	0.09 per cent	0.12 per cent	0.15 per cent
2.95	2.62	2.30	1.76	1.72
2.90	2.61	2.18	1.77	1.72
2.74	2.34	2.16	1.68	1.77
2.54	2.25	2.07	1.68	1.79
2.38	2.26	1.99	1.65	1.72
2.40	2.24	1.91	1.62	1.68
2.40	2.24	1.82	1.59	1.59
2.40	.....	1.78	1.63	1.60
.....	.....	1.79	1.61	1.61
.....	.....	1.79	1.61	1.62

Similar variations, though not so marked, were encountered with Georgia kaolin, but not with North Carolina kaolin and

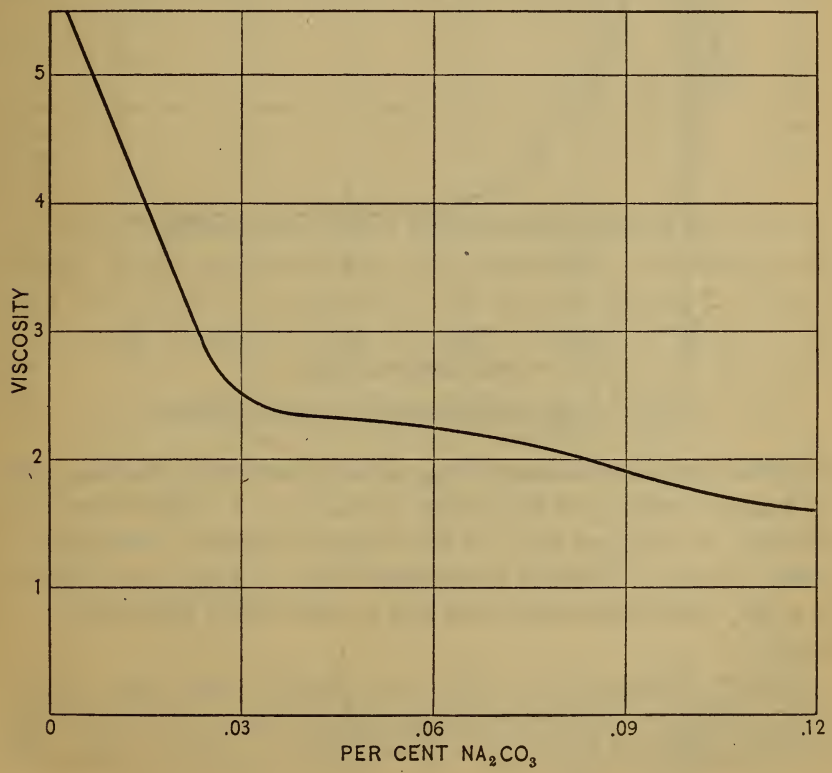

FIG. 10.—*Effect of sodium carbonate on Florida kaolin body*

Tennessee ball clay. Although the slips in each case were shaken, allowed to stand for as long as 72 hours after the alkali was added, and again shaken before the viscosity determination was made, the additional disturbance caused by pouring the slip evidently caused a further liquefying effect. Hence the preliminary drying to 110° C did not seem to prevent these changes.

Sodium Carbonate Series (*Fig. 10*).—It is observed from this

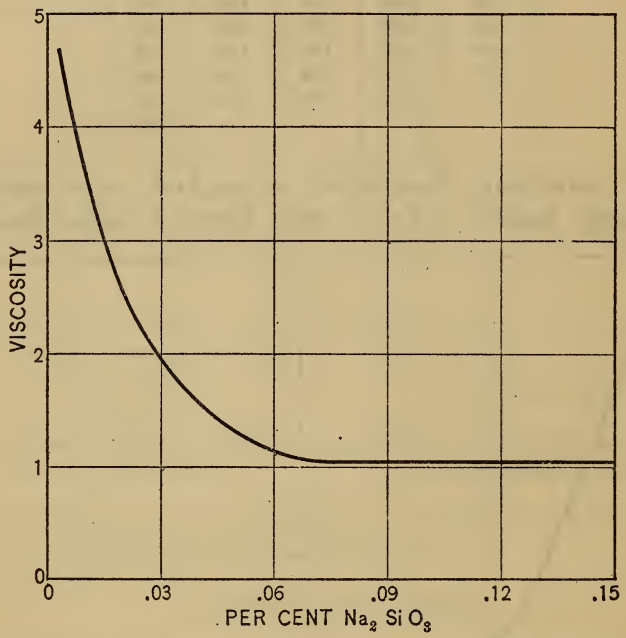

FIG. 11.—*Effect of sodium silicate on Florida kaolin body*

diagram that the viscosity drop is very decided. Starting with an initial viscosity so high that it could not be determined, the addition of 0.03 per cent of the reagent brought down the viscosity to 2.45. Further increments tend to lower the viscosity at a very much decreased rate, but a well-defined minimum is not reached.

Sodium Silicate Series (*Fig. 11*).—In this case again the viscosity drop is very great with 0.03 and 0.06 per cent of the alkali. Further additions appeared to bring about no more changes with

additions as high as 0.15 per cent. The sodium silicate proved to be more effective in its action than the carbonate.

In the course of this work it was observed that upon subjecting any of the slips to a vacuum large volumes of air were expelled even in completely deflocculated suspensions. It was thought desirable, therefore, to subject some of the slips to the vacuum treatment and to compare the viscosity with the previous value. These results are compiled in Table 3.

TABLE 3

Kind of body	Percentage addition of Na_2SiO_3	Viscosity before the vacuum treatment	Viscosity after the vacuum treatment
Georgia kaolin	0.03	2.60	2.94
Do	.06	2.32	2.72
Tennessee ball clay	.03	1.14	1.22
Do	.06	1.08	1.08
North Carolina kaolin	.03	1.43	1.50
Do	.06	1.34	1.39
Do	.12	1.33	1.40
Florida kaolin	.03	1.91	3.00
Do	.06	1.08	1.08

It would appear, thus, that a considerable amount of air is entrapped within the fine-grained clays, especially in the case of the more plastic ones. It seems also that this air appears to be held in a state of absorption, since no contraction in the volume of the slip was noted. The effect was more prominent with the lower alkali concentrations and with the Georgia and Florida kaolins.

In addition to these body mixtures another body, B, was prepared containing three of these clays in the following proportions:

	Per cent.
Feldspar	21
Flint	34
North Carolina kaolin	20
Florida kaolin	20
Tennessee ball clay	5

The initial slip in this case contained 55 per cent of solids. Only one series was run using sodium carbonate. The results are presented graphically in Fig. 12. The drop to minimum viscosity—from 3.5 to 1.25—with 0.06 per cent is quite marked, and

the rise toward another maximum is clearly indicated. The coagulating tendency is very gradual, and hence the deflocculation range is of generous extent.

A commercial casting body obtained through the courtesy of a Trenton firm was likewise studied. The composition of the body was not given. In this case a mixture of sodium carbonate and sodium silicate in equal parts was used. The results of this test are shown graphically in Fig. 13. It appears that this body, owing to its high ball clay content, requires for maximum deflocculation a content of 0.2 per cent of the reagent mixture. The

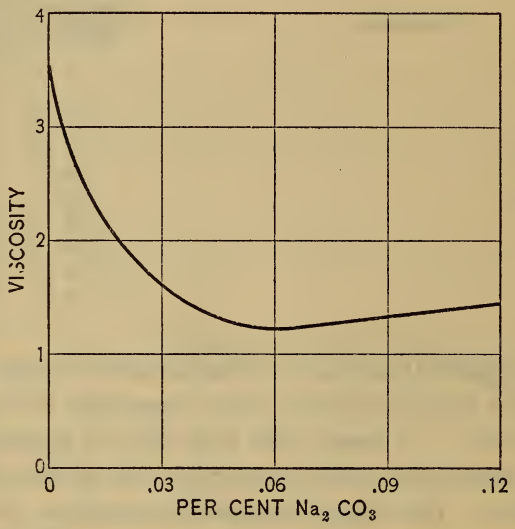

FIG. 12.—*Effect of sodium carbonate upon body B*

viscosity of the slip which contained 66.69 per cent solids, without any addition of alkali, could not be determined. The viscosity drop, corresponding to an alkali addition from 0.1 to 0.2 per cent, is quite marked—from 4.17 to 1.5. After maximum deflocculation is attained the condition of the slip appears to be quite constant and there is no evidence of any coagulating tendency. About 0.15 per cent of the reagents would appear to be the proper concentration for casting purposes, considering no other factors, such as after-stiffening.

VII. VISCOSITY OF CLAY MIXTURES WITHOUT ADDITION OF ALKALI

Our attention has been called to the fact that there is a certain interaction of mixtures of different clays as brought out by viscosity measurements. T. G. McDougal has informed us of interesting results obtained in this connection. In order to test out this point and to determine whether the addition of one clay slip to another caused regularly progressive or discontinuous changes

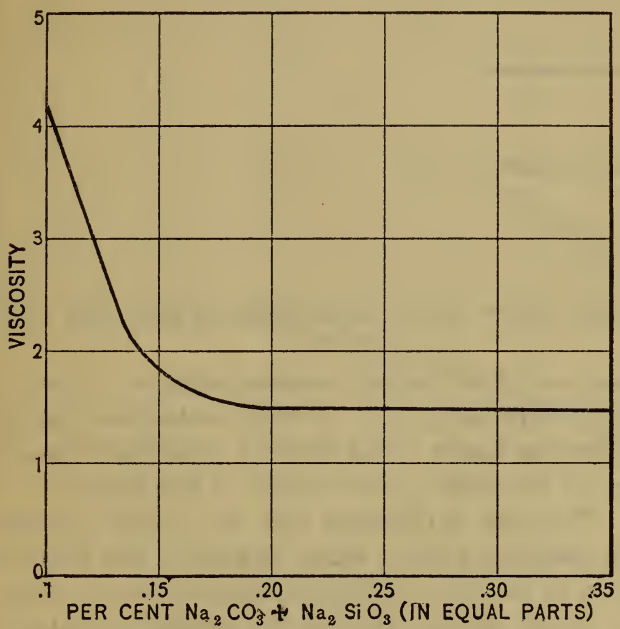

FIG. 13.—*Effect of sodium carbonate and sodium silicate mixture on Trenton casting body*

in viscosity, four porcelain body slips were prepared of North Carolina kaolin, Georgia kaolin, Tennessee ball clay, and Florida kaolin. The body composition was the same as that previously employed. The contents of solids in the above order were 53.8, 53.64, 53.67, and 42.27 per cent. The viscosities of these bodies were found to be 1.21, 1.08, 1.80, and 2.94. The mixtures were then made so that the North Carolina kaolin body slip was blended with each of the other three bodies in the proportion of 1:1, 2:1,

3:1, and 4:1, on the basis of dry weights. The contents of solids for the various blends were as follows:

TABLE 4

Mixture of bodies	Ratio of North Carolina kaolin to other body	Percentages of solids in slip
North Carolina-Georgia kaolins	1:1	53.52
Do	2:1	53.55
Do	3:1	53.78
Do	4:1	53.26
North Carolina-Tennessee ball	1:1	54.02
Do	2:1	53.60
Do	3:1	53.56
Do	4:1	53.26
North Carolina-Florida kaolin	1:1	51.36
Do	2:1	53.69
Do	3:1	53.82
Do	4:1	53.88

The bodies before having been made up into slips were dried at 110° C.

The results of the viscosity determinations of these series are shown graphically in Fig. 14. It will be observed that the North Carolina-Georgia kaolin series shows a practically linear relation, indicating no interfering phenomena in the mixture of the two systems. The case is different with the North Carolina kaolin-Tennessee ball clay series. Here, as long as the kaolin predominates, down to the ratio of 2:1, no marked change occurs. With an excess of ball clay in the ratio 1:1 sudden coagulation occurs, and the viscosity rises rapidly to a value considerably above that reached by either body slip alone. In the North Carolina-Florida kaolin series the viscosity rises with the increase in the more plastic constituents, but shows a decided drop when the ratio 1:1 is reached. The reason for this decrease is not evident. These results are sufficient to show that interaction between different clays occurs in slips, and these may have decided influence upon the behavior in the casting.

VIII. ABSORPTION OF ALKALIES BY CLAY

In order to determine the degree to which clays absorb alkaline salts, mixtures of Florida kaolin, Georgia kaolin, and Georgia kaolin with 50 per cent flint were treated with solutions of NaOH and Na_2CO_3 of different concentrations. The procedure consisted in weighing out samples of the materials, adding a constant volume of the solution, and rapidly filtering by suction in a vessel containing air previously passed through KOH. By titrating for

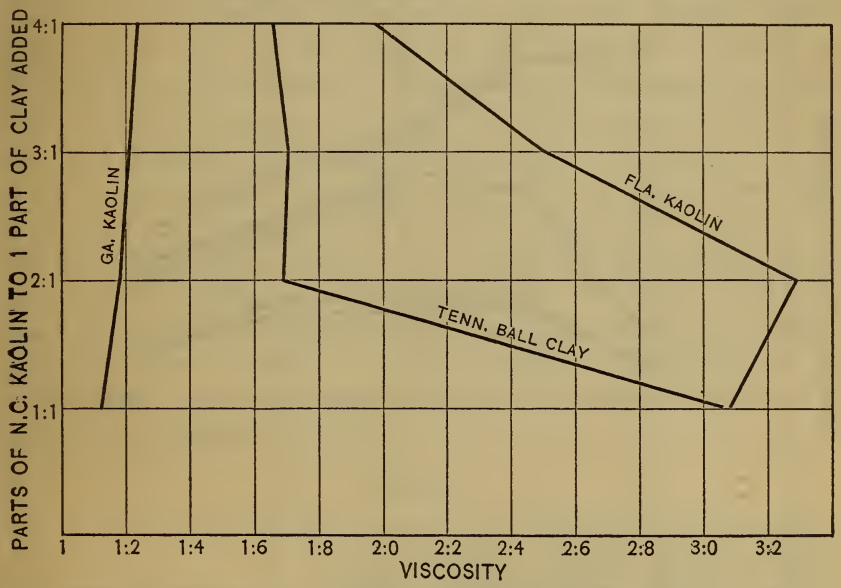

FIG. 14.—*Viscosity of clay mixtures*

the alkali content per cubic centimeter of the original solution and in the filtrate the amount absorbed was readily found. The results of this work are shown in Fig. 15. In this diagram the alkali content is expressed in terms of percentage of the dry clay. The maximum absorption of Na_2CO_3 in Florida kaolin is 0.16 per cent of alkali added, being 40 per cent of 0.4. The amount absorbed from the more dilute solutions increases with the concentration and appears to remain constant at the above value.

The same clay mixture absorbed a far greater amount of NaOH, namely, 0.28 per cent, or 56 per cent of 0.5. Since the absorp-

tion with both 0.4 and 0.5 per cent is practically the same, it appears as if the amount absorbed approached constancy, though it is but reasonable to suppose that some reaction with the silica of the clay should occur, especially with higher concentrations of NaOH.

With the Georgia kaolin-flint mixture the absorption with 0.4 and 0.5 per cent Na_2CO_3 added is practically the same, being 0.23

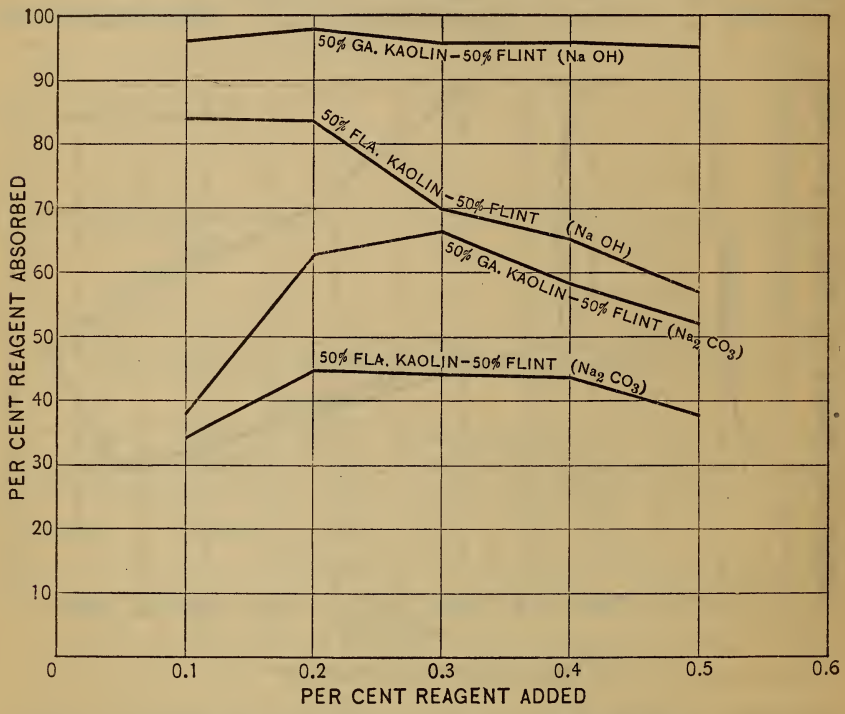

FIG. 15.—*Absorption of alkali by clay-flint mixtures*

and 0.26 per cent, respectively. These values, therefore, appear to be practically constant for this clay.

The Georgia kaolin-flint mixture appeared to absorb about 95 per cent of the NaOH added for practically all concentrations. This indicates chemical reaction with the clay, and we are evidently not dealing here with a case of simple absorption.

From these data it seems, therefore, that absorption of the alkalies plays an important rôle in casting slips. The greater absorption of NaOH is probably responsible for the greater

effectiveness of sodium silicate in the liquefaction brought about. Whether or not the content of the Na_2CO_3 absorbed is a criterion of the degree of dispersion of clays remains to be demonstrated, but the indications are that it might do so.

IX. TENSILE STRENGTH TESTS OF BODY MIXTURES

In order to throw light upon the effect of the alkaline reagents in regard to the structure of cast bodies, the tensile strength of briquettes dried at 110° C and formed by casting in suitable plaster molds was determined. The same single clay bodies studied before were used for this work and five series of 10 briquettes were made from each body. These were (*a*) briquettes cast from the slip without addition of reagent; (*b*) briquettes cast from the slip with addition of Na_2CO_3 corresponding to the point of maximum deflocculation (minimum viscosity); (*c*) test pieces cast from slip with a concentration of Na_2CO_3 equivalent to a point to the left of minimum viscosity; (*d*) briquettes from slip with an addition of Na_2SiO_3 necessary to produce maximum deflocculation; (*e*) specimens from slip containing an amount of Na_2SiO_3 corresponding to a point to the left of minimum viscosity.

The same tests were made also with the casting body B. The results are compiled in Table 5.

TABLE 5

Body containing as clay	Without reagents (lbs. per sq. in.)	Na_2CO_3. Maximum deflocculation (lbs. per sq. in.)	Na_2CO_3. Less than maximum deflocculation (lbs. per sq. in.)	Na_2SiO_3. Maximum deflocculation (lbs. per sq. in.)	Na_2SiO_3. Less than maximum deflocculation (lbs. per sq. in.)
North Carolina kaolin	14.9	17.8	14.0	14.7	17.2
Georgia kaolin	68.0	87.1	78.6	100.7	89.7
Tennessee ball clay	102.5	153.8	136.3	168.3	131.3
Florida kaolin	65.7	70.5	62.4	56.5	62.5
Body B	.....	67.33	73.2	59.0	91.1

From these results it appears first that the strength of cast bodies containing the alkaline reagents is greater than that of the bodies cast without any additions. Second, in bodies containing but a single clay, the state of maximum deflocculation does not,

as might be expected, result in weaker structure than when the bodies are carried to a point to the left of minimum viscosity; in fact, the opposite is the case. It is possible, of course, that owing to the small volume of the briquettes the calcium sulphate taken up from the molds might have exercised some influence.

X. THE CONSTANT OF THE GENERAL VISCOSITY FORMULA

Owing to the fact that the general formula makes the assumption that the viscosity of a dispersed system composed of spherical particles is a linear function of the volume of disperse phase, which we know from previous investigations is not true for clays in high concentrations, it was thought desirable to determine the constant of the expression for several concentrations of clay slips. For this purpose the exceedingly fine-grained washed Florida kaolin was used. Three concentrations were prepared containing, respectively, 10.58, 18.96, and 21.23 per cent of solids. The viscosities as measured by the efflux tube were 1.043, 1.55, and 2.83. Calculating the volume of the dispersed matter by dividing by the specific gravity of the clay, 2.6, and the volume of the system, we obtain for

Case I

$$1.043 = (1 + \frac{4.07}{93.49} k);$$

solving for k we have the value $k = 1$.

Case II

$$1.55 = (1 + \frac{7.29}{88.3} k);$$

solving, $k = 6.25$.

Case III

$$2.83 = (1 + \frac{8.15}{86.92} k);$$

solving, $k = 19.4$.

The value of k therefore increases rapidly with the content of solid and in using this relation for the calculation of the viscosity for any given concentration, or vice versa, it will be necessary to compute this value for a series of concentrations so as to obtain a curve

expressing this relation. In case such a calculation is applied to a casting slip the percentage content of alkali in terms of the dry weight of the materials must be kept constant or else discrepancies will appear.

XI. THE TIME FACTOR

The change in the viscosity of slips with time is a very important factor in casting practice. Considerable trouble ensues frequently owing to the use of variously aged slip. Thus in one case a slip proved to work very satisfactorily after 24 hours blunging, but

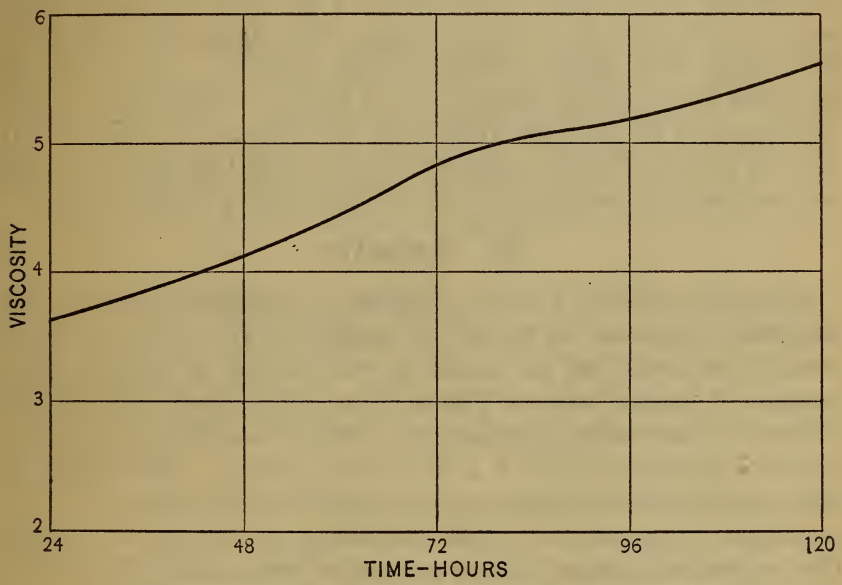

FIG. 16.—*Change in the viscosity of a body slip with time*

showed a decided "livery" consistency, due to coagulation, after three days. This phenomenon was constantly met with in the present work and was not overcome by the predrying of the clay body at 110° C. It seemed to be evident also that the slips containing alkali just sufficient to bring about maximum deflocculation, or less than this amount, were more apt to show fluctuation in viscosity than those containing more than the required amount. The time factor is explained, first, by the fact that the action of the alkalies upon the dispersed matter is often quite slow unless vigorous agitation is kept up constantly. Second, the concentration of

alkali may change also because of absorption and reaction with silica or the soluble sulphates. The latter salts play an especially important part in the case of ball clays, which, as is well known, may diminish the liquefying action of the alkalies in a very decided manner or require the addition of an excess of the alkali. According to the nature of the clays and the content of the reagents the time effect may consist in further deflocculation or in coagulation of the slip. Clay slips containing no alkaline reagents are subject to even greater variations in viscosity than casting slips. The accompanying diagram (Fig. 16) shows the gradual coagulation of a practical casting body containing 0.1 per cent of a mixture of sodium carbonate and sodium silicate. This phenomenon does not take place with higher concentrations of alkali. It is necessary therefore in preparing casting slips to know the time effect so as to counteract it by properly regulating the content of reagents. It is quite possible that the organic colloids of the ball clay may tend to exercise a protective influence on the stability of the system.

XII. SUMMARY

It has been shown that the washing of kaolinitic clays may be decidedly improved as far as the quality of the product is concerned by adding to the water in the blunger a definite small amount of caustic soda or a mixture of caustic soda and sodium silicate. This makes possible more complete sedimentation of the granular impurities which it is desired to remove. This treatment improves the color of most clays, enriches their content in clay substance, decreases the drying shrinkage, but tends to increase the burning shrinkage. Clays containing iron in the form of finely divided ferric oxide can not be treated successfully by this process.

The electrical osmosis process plays no important part in the purification of clays. Its function is that of mechanically depositing particles in suspension upon the positive electrode. It thus replaces the filter press, and if the latter is of a modern improved type any advantage resulting from continuous and automatic operation will be more or less neutralized. The higher the voltage of the current employed the denser will be the deposit of clay and the lower the water content. The preliminary sedimentation process, using caustic soda or other electrolytes, seems to be the real feature of the osmose process. The electrical method of separa-

tion can not remove finely divided ferric oxide. It also deposits with the clay any finely divided quartz which may be in suspension.

The efflux viscosimeter appears to be satisfactory for the technical study of casting slips. The kinetic and temperature corrections applied in precise measurements are not necessary for the purpose in view.

Sodium silicate is a more effective reagent as far as the reduction of viscosity is concerned than sodium carbonate.

North Carolina kaolin in suspension is not influenced by the reagents in question in a marked manner, because of its comparative coarseness.

Georgia kaolin has a far greater initial viscosity than the North Carolina kaolin and appears to be very sensitive to additions of sodium carbonate. It shows a well-defined minimum of short range, which turns toward a maximum. Its range at minimum viscosity is greater when sodium silicate is used.

Tennessee ball clay No. 3 gives no indication of a decided minimum viscosity point.

Florida kaolin responds decidedly to the addition of sodium carbonate, but a well-defined minimum is not reached, probably due to the comparatively large amount of pseudoemulsoid or lyophile substance produced. With sodium silicate the viscosity decrease is equally great, with no tendency to approach another maximum value.

A large volume of air seems to be absorbed in clay slips, the removal of which increases the viscosity. Thorough and vigorous stirring of the slip therefore seems essential, and exhaustion by vacuum might be beneficial. The effect of the entrapped air was more prominent with lower alkali concentrations and with the Georgia and Florida kaolins.

A body containing North Carolina kaolin, Florida kaolin, and Tennessee ball clay responded well to the addition of sodium carbonate, but showed a turn toward greater viscosity (recoagulation) for additions greater than 0.06 per cent.

A commercial slip fairly high in English ball clay showed a rapid drop in viscosity, but required a much higher percentage of the reagent mixture than the single clay bodies. The viscosity seemed to remain constant at the minimum value. It is possible that

this condition is due to the presence of organic colloids which exercise a protective influence.

Interaction occurs between different clays with respect to viscosity changes independent of the alkali additions, and these are not necessarily proportional to the ratios of the admixed clays or regular in character. It is important therefore to know just what this interaction is, since it is quite possible that some clays may have a detrimental effect upon the others in making up the casting body. The ball clay content in a casting slip should be reduced to the minimum.

Absorption of the alkaline reagents plays an important rôle in casting slips. Sodium hydroxide is absorbed to a far greater extent than the carbonate and probably combines chemically with the clay.

The tensile strength of cast bodies containing alkali additions may be greater than that of the same materials cast without these reagents. Single clay body slips used in the state of maximum deflocculation do not seem to be weaker than when the suspensions are only carried to a point to the left of minimum viscosity.

The general formula, $n_1 = n\ (1 + kf)$, where f = ratio of volume of dispersed particles to total volume of system and in which k is determined for each of a series of concentrations, might prove useful for interpolation purposes, provided the alkali addition is kept constant.

Casting bodies with low concentrations of alkali are more apt to change their viscosity with time than those containing larger additions.

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